Inter (Part-I) 2017

Chemistry	Group-I	PAPER: I
Time: 2.40 Hours	(SUBJECTIVE TYPE)	Marks: 68

SECTION-I

2. Write short answers to any EIGHT (8) questions: (16)

(i) Why 23 g of Na and 238 g of uranium have equal number of atoms in them?

Ans 23 g of Na:

1 mole of Na = 6.02×10^{23} atoms of Na

238 g of U:

1 mole of U = 6.02×10^{23} atoms of U

Since, equal number of gram atoms (moles) of different elements contain equal number of atoms.

Hence, 1 mole (23 g) of sodium and 1 mole (238 g) of uranium contain equal number of atoms which is 6.02×10^{23} atoms.

(ii) How Mg-atom is twice heavier than that of C-atom?

Ans As the atomic mass of Mg (24) is twice the atomic mass of carbon (12), therefore, Mg atom is twice heavier than that of C-atom.

(iii) Why 2 g of H_2, 16 g of CH_4 and 44 g of CO_2 occupy separately the volumes of 22.414 dm^3 although the sizes and masses of molecules of these three gases are very different from each other?

Ans 2g of H_2:

1 mole of $H_2 = 6.02 \times 10^{23}$ molecules of H_2

16 g of CH_4:

1 mole of $CH_4 = 6.02 \times 10^{23}$ molecules of CH_4

144 g of CO_2

1 mole of $CO_2 = 6.02 \times 10^{23}$ molecules of CO_2

Though H_2, CH_4 and CO_2 have different masses yet they have the same number of moles and molecules. Therefore, 2g

of H_2, 16 g of CH_4 and 44 g of CO_2 occupy separately the volumes of 22.414 dm^3.

(iv) Write down the four main characteristics of solvent selected for crystallization of a compound.

Ans The four main characteristics of solvent selected for crystallization of a compound are:

1. It should dissolve a large amount of the substance at its boiling point and only a small amount at the room temperature.
2. It should not react chemically with the solute.
3. It should either not dissolve the impurities or the impurities should not crystallize from it along with the solute.
4. On cooling, it should deposit well-formed crystals of the pure compound.

(v) How chemical characterization of a compound is done?

Ans A complete chemical characterization of a compound must include both qualitative and quantitative analysis. In qualitative analysis, the chemist is concerned with the detection or identification of the elements present in a compound. Whereas, in quantitative analysis, the relative amounts of the elements are determined.

(vi) What do you mean by solvent extraction? Which law controls it?

Ans Solvent extraction is an equilibrium process and follows the distribution law or partition law. This law states that solute distributes itself between two immiscible liquids in a constant ratio of concentrations irrespective of the amount of solute added.

(vii) Why do we feel comfortable in expressing the densities of gases in units of g dm^{-3} rather than g cm^{-3}, a unit which is used to express the densities of liquids and solids?

Ans If gas densities are expressed in g cm^{-3}, then the values will be very small. When we express the densities in g dm^{-3}, then the values of the densities become reasonable to be

expressed. Therefore, we feel comfortable in expressing the densities of gases in the units of g dm^{-3} rather than in g cm^{-3}.

(viii) Derive Charles's law by kinetic equation of gases.

Ans Consider the equation,

$$PV = \frac{2}{3}kT$$

which has just been derived,

$$PV = \frac{2}{3}kT$$

$$V = \frac{2}{3}\frac{kT}{P} = \left(\frac{2k}{3P}\right)T$$

At constant pressure,

$$\frac{2}{3}\frac{k}{P} = k'' \text{ (a new constant)}$$

Therefore,

$$V = k''T$$

$$\frac{V}{T} = k' \qquad \text{(which is Charles' law)}$$

(ix) Derive molecular mass of a gas by general gas equation.

Ans This equation shows that if we have any quantity of an ideal gas then the product of its pressure and volume is equal to the product of number of moles, general gas constant and absolute temperature. This equation is reduced to Boyle's law, Charles's law and Avogadro's law, when appropriate variables are held constant.

$PV = nRT$, when T and n are held constant,

$PV = k$ (Boyle's law)

$V = R\frac{nT}{P}$, when P and n are held constant,

$V = kT$ (Charles' law)

$V = R\frac{nT}{P}$, when P and T are held constant,

$V = kn$ (Avogadro's law)

For one mole of a gas, the general gas equation is:

$$PV = RT \quad \text{or} \quad \frac{PV}{T} = R$$

It means that ratio of PV to T is a constant quantity (molar gas constant).

Hence,

$$\frac{P_1V_1}{T_1} = R \qquad \frac{P_2V_2}{T_2} = R$$

Therefore,

$$\therefore \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

(x) What is Henderson's equation and for which purpose is it used?

Ans Henderson's equation shows that two factors evidently govern the pH of a buffer solution, *i.e.*,

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

The best buffer is prepared by taking equal concentration of salt and acid. So, pH is controlled by pK_a of the acid.

(xi) What are applications of buffer in daily life?

Ans The buffer capacity of a solution is the capability of a buffer to resist the change of pH. It can be measured quantitatively that how much extra acid or base, the solution can absorb before the buffer is essentially destroyed.

(xii) Derive ionic product of water and what is its value at 25°C?

Ans Let us have an acid HA, and it gives protons to water in a reversible manner. H_3O^+ gives proton to A and is an acid, but A accepts H^+ from H_3O^+ and act as a conjugate base of HA.

$$\underset{\text{acid}}{HA} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{conjugate acid of } H_2O}{H_3O^+} + \underset{\text{conjugate base of HA}}{A^-}$$

Now,

$$K_c = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \text{ or } K_a = \frac{[H^+][A^-]}{[HA]}$$

In case A^- is dissolved in water, the equation for hydrolysis of conjugate base A^- will be,

$$\underset{\text{base}}{A^-} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{acid}}{HA} + \underset{\text{base}}{OH^-}$$

So, its

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

Let us multiply two expressions for K_a and K_b,

$$K_a \times K_b = \frac{[H^+][A^{1-}]}{[HA]} \times \frac{[OH^-][HA]}{[A^{-1}]}$$

Or $\quad K_a \times K_b = [H^+][OH^-]$

Or $\quad K_a \times K_b = K_w$

This equation is useful in the sense that if we know K_a of the acid, we can calculate K_b for the conjugate base and vice versa. The value of K_w is constant at a given temperature. *i.e.*, 10^{-14} at 250°C and less then 14 at higher temperatures.

3. Write short answers to any EIGHT (8) questions: (16)

(i) Why ice floats at surface of liquid water?

Ans Ice floats at surface of liquid water because density of ice is less than water.

(ii) Describe cleaning action of soaps and detergents on the basis of H-bonding.

Ans Cleaning action of soaps and detergents is that the carbon chain dissolves in oil and the ionic end dissolves in water. Therefore, it forms emulsion in water and helps in dissolving the dirt when we wash our clothes.

(iii) Why boiling point of water varies from sea-level to higher places?

Ans Water can be made to boil at any temperature by changing the external pressure. As it varies from sea-level to higher places, the water requires greater amount of heat to equalize its vapour pressure to external pressure. In this way, boiling point is raised.

(iv) Define isomorphism with one example.

Ans **Isomorphism:**

It is a phenomenon in which two different substances exist in the same crystalline form. The different substances are isomorphs.

e.g., $NaNO_3$, $KNO_3 \longrightarrow$ rhombohedral

Zn, Cd $\longrightarrow$ hexagonal

Cu, Ag $\longrightarrow$ cubic

(v) **Give products formed due to decay of neutrons.**

Ans When neutrons are used as projectiles, they can carry out the nuclear reactions. A fast neutron ejects an α-particle from the nucleus of nitrogen atom and boron is produced, although with α-particles.

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{11}_{5}B + ^{4}_{2}He$$

(vi) **Give two postulates of Planck's theory.**

Ans Two postulates of Planck's theory are:

1. Energy is not emitted or absorbed continuously. Rather, it is emitted or absorbed in a discontinuous manner and in the form of wave packets. Each wave packet or quantum is associated with a definite amount of energy. In case of light, the quantum of energy is often called photon.
2. The amount of energy associated with a quantum of radiation is proportional to the frequency (ν) of the radiation. Frequency is the number of waves passing through a point per second.

$$E \propto \nu$$
$$E = h\nu$$

Where 'h' is a constant known as Planck's constant and its value is 6.626×10^{-34} Js. It is, in fact, the ratio of energy and the frequency of a photon.

(vii) **Define Stark's effect.**

Ans When the excited hydrogen atoms are placed in an electrical field, then similar splitting of spectral lines takes place which is called "Stark's effect".

(viii) **Describe (n + *l*) rule for distribution of electrons.**

Ans According to (n + *l*) rule for distribution of electrons, subshells are arranged in the increasing order of (n + *l*) values and if any two subshells have the same (n + *l*) values, then that subshell is placed first whose n value is smaller.

(ix) **Give conjugate solution with one example.**

Ans Each liquid layer is a saturated solution of the other liquid. Such solutions are called conjugate solutions.

(x) Why NaCl and KNO_3 are used to lower the melting points of ice?

Ans Because both NaCl and KNO_3 lower the vapour pressure and hence, depress the freezing point of ice.

(xi) Calculate oxidation number of 'S' in H_2SO_4.

Ans Oxidation number of oxygen = –2

Hence, for $O_4 = -8$

Oxidation number of Hydrogen = +1

Hence, for $H_2 = +2$

By adding both,

$$+2 - 8 = +6$$

Hence, the sulphur has +6 oxidation number in Sulfuric Acid (H_2SO_4).

(xii) How impure copper can be purified by electrolytic process?

Ans Impure copper is made the anode and a thin sheet of pure copper is made the cathode. Copper sulphate solution is used as an electrolyte. The atoms of Cu from Cu^- anode are converted to Cu^{2+} ions and migrate to cathode which is made up of pure Cu. In this way, Cu anode is purified. Impurities are left at anode.

4. Write short answers to any SIX (6) questions: (12)

(i) Ionization energy decreases down the group. Why?

Ans The ionization energy of the element is the minimum energy required to remove an electron from its gaseous atom to form an ion. The process is called ionization *e.g.,*

$$Mg \longrightarrow Mg^+ + e^-$$

In groups, the ionization energy decreases in spite of the increase in proton number or nuclear charge.

(ii) Ionic compounds do not show the phenomena of isomerism. Why?

Ans Ionic bond is electrostatic. It is non-directional, so ionic compounds do not show the phenomena of isomerism.

(iii) Sigma bond is stronger than pi-bond. Why?

Ans It is because sigma bond is formed by head-to-head approach and electronic cloud density is symmetrically

distributed along the bond but π bond is formed by parallel overlapping of two half-filled p-orbitals. The electronic cloud density is not symmetrically along bond axis. It has two regions of electronic cloud density above and below the bond axis. Therefore, π bond is more diffused.

(iv) Define ionic and covalent radii.

Ans **Ionic Radius:**

It is the radius of an ion considered spherical in shape.

Covalent Radius:

It is half the length of a covalent bond between two atoms.

(v) Define enthalpy of neutralization and enthalpy of combustion.

Ans **Enthalpy of Neutralization:**

The standard enthalpy of neutralization is the amount of heat evolved when one mole of hydrogen ions [H] from an acid, react with one mole of hydroxide ions from a base to form one mole of water.

Enthalpy of Combustion:

The standard enthalpy of combustion of a substance is the amount of heat evolved when one mole of a substance is completely burnt in excess of oxygen under standard conditions. It is denoted by ΔH^0_c.

(vi) A catalyst is specific in its action. Justify.

Ans A catalyst is specific in its action. When a particular catalyst works for one reaction, it may not necessarily work for any other reaction. If different catalysts are used for the same reactant then the products may change. For example,

Formic acid is decomposed by Al_2O_3 to H_2O and CO while Cu causes its decomposition to H_2 and CO_2.

$$HCOOH \xrightarrow{Al_2O_3} H_2O + CO$$

$$HCOOH \xrightarrow{Cu} H_2 + CO_2$$

(vii) Define homogeneous and heterogeneous catalysis.

Ans **Homogeneous Catalysis:**

In homogeneous catalysis, the catalyst and the reactants are in the same phase and the reacting system is

homogeneous throughout. The catalyst is distributed uniformly throughout the system.

Heterogeneous Catalysis:

In heterogeneous catalysis, the catalyst and the reactants are in different phases. Mostly, the catalysts are in the solid phase, while the reactants are in the gaseous or liquid phase.

(viii) Rate of reaction increases by increasing surface area of reactants. Why?

Ans The increased surface area of reactants, increases the possibilities of atoms and molecules of reactants to come in contact with each other and the rates enhance. For example, *Al* foil reacts with NaOH moderately when warmed, but powdered *Al* reacts rapidly with cold NaOH and H_2 is evolved with frothing.

$$2Al + 2NaOH + 6H_2O \longrightarrow 2NaAl(OH)_4 + 3H_2$$

(ix) What is the effect of temperature on energy of activation of a reaction?

Ans All the molecules of a reactant do not possess the same energy at a particular temperature. Most of the molecules will possess average energy. A fraction of total molecules will have energy more than the average energy. As the temperature increases, the number of molecules in this fraction also increases.

SECTION-II

NOTE: Attempt any Three (3) questions.

Q.5.(a) Ethylene glycol is used as automobile antifreeze. It has 38.7% carbon, 9.7% hydrogen and 51.6% oxygen. Its molar mass is 62.1 grams mol^{-1}. Determine its empirical and molecular formula. (4)

Ans Percentage of:

Carbon = 38.7 g

Hydrogen = 9.7 g

Oxygen = 51.6 g

Molar Mass = 62.1 g mol^{-1}

Share of Mass of:

Carbon = 12 g mol^{-1}

Hydrogen = 1.008 g mol^{-1}

Oxygen = 16 g mol^{-1}

Number of Moles of:

$$\text{Carbon} = \frac{38.7\text{ g}}{12\text{ g mol}^{-1}} = 3.23$$

$$\text{Hydrogen} = \frac{9.7\text{ g}}{1.008\text{ g mol}^{-1}} = 9.62$$

$$\text{Oxygen} = \frac{51.6\text{ g}}{16\text{ g mol}^{-1}} = 3.23$$

Atomic ratio is obtained by dividing the moles with 3.23, *i.e.*, the smallest ratio

$$\text{C} : \text{H} : \text{O}$$

$$\frac{3.23}{3.23} : \frac{9.62}{3.23} : \frac{3.23}{3.23}$$

$$1 : 3 : 1$$

(b) Elucidate the term ionic solids. Write down three properties of ionic solids. (4)

Ans Ionic Solids:

Definition:

"Crystalline solids which consist of positively and negatively charged ions that are held together through strong electrostatic forces of attraction (ionic bonds) are called ionic solids."

Examples:

NaCl, KBr, $NaNO_3$, etc.

Properties:

1. Physical state:

They are solids at room temperature under ordinary conditions of temperature and pressure. They never exist in the form of liquids or gases.

2. Stability:

Ionic crystals are very stable compounds. This greater stability is due to the fact that cations and anions are held together through very strong forces of attraction. Therefore, very high energy is required for the separation of cations and anions form each other. This high stability of the ionic crystals explain their:

(i) Hardness,

(ii) Low volatility,

(iii) High melting and boiling points.

3. **Molecular existence:**

Ionic solids do not exist as individual neutral independent molecules. Therefore, we always represent ionic solids in terms of formula units.

Q.6.(a) State Graham's law of diffusion. Give its experimental verification. (4)

Ans Graham's Law of Diffusion:

This law can also be very easily verified in the laboratory by noting the rates of diffusion of two gases in a glass tube, when they are allowed to move from opposite ends as shown in the following figure. Two cotton plugs soaked in HCl and NH_3 solutions are introduced in the open ends of 100 cm long tube simultaneously. HCl molecules travel a distance of 40.5 cm while NH_3 molecules cover 59.5 cm in the same duration. They produce dense white fumes of ammonium chloride at the point of junction. So,

$$\frac{r_{NH_3}}{r_{HCl}} = \frac{\sqrt{M_{HCl}}}{\sqrt{M_{NH_3}}}$$

$$\frac{59.5}{40.5} = \frac{\sqrt{36.5}}{\sqrt{17}}$$

$$1.46 = 1.46$$

Hence, the law is verified.

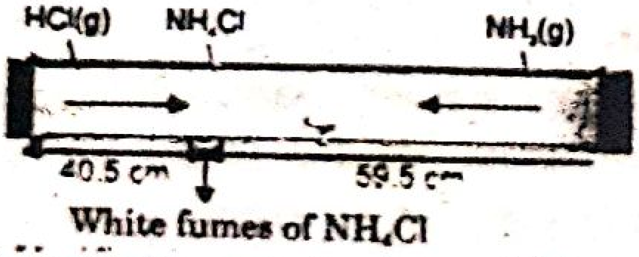

Fig. Verification of Graham's law of diffusion.

(b) Derive an expression to calculate the radius of revolving electron in nth orbit by Bohr's model of atom. (4)

Ans

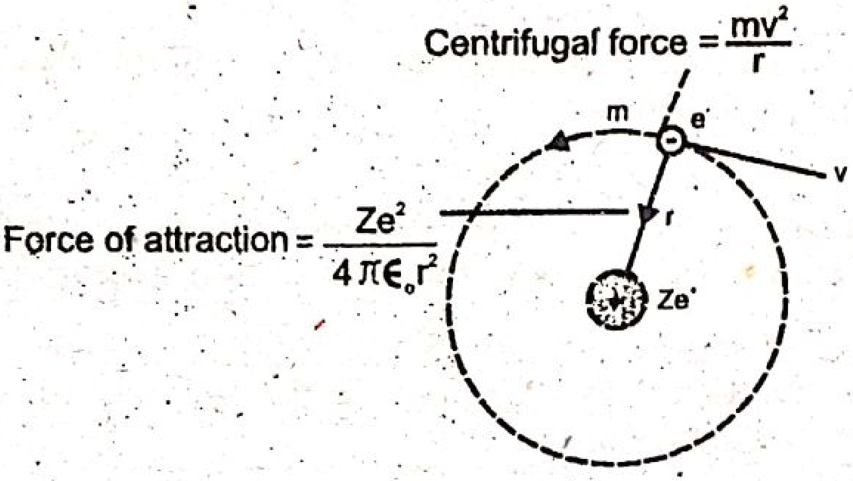

Fig. Electron revolving in an atom with nuclear charge Ze^+ (If Z = 1, then the picture is for H-atom)

Let m be the mass of electron, r is the radius of the orbit and v is the velocity of the revolving electron. According to Coulombs law, the electrostatic force of attraction between the electron and the nucleus will be given by the following formula:

$$\frac{Ze^+.e^-}{4\pi\epsilon_o r^2} = \frac{Ze^2}{4\pi\epsilon_o r^2}$$

ϵ_o is the vacuum permittivity and its value is $8.84 \times 10^{-12} C^2 J^{-1} m^{-1}$. This force of attraction is balanced by the $\frac{mv^2}{r}$.

Therefore, for balanced conditions, we can write:

or $$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_o r^2}$$

$$mv^2 = \frac{Ze^2}{4\pi\epsilon_o r} \qquad (I)$$

Rearranging the above equation (I),

$$r = \frac{Ze^2}{4\pi\epsilon_o mv^2} \qquad (II)$$

According to equation (II), the radius of a moving electron is inversely proportional to the square of its velocity. It conveys

the idea, that electron should move faster nearer to the nucleus in an orbit of smaller radius. It also tells, that if hydrogen atom has many possible orbits, then the promotion of electron to higher orbits makes it move with less velocity.

Q.7.(a) Describe postulates of valence shell electron pair repulsion theory. (4)

Ans For Answer see Paper 2016 (Group-II), Q.7.(a).

(b) What is Hess's law of constant heat summation? Explain this law with the help of two examples. (4)

Ans For Answer see Paper 2016 (Group-II), Q.7.(b).

Q.8.(a) Explain discharging and recharging in lead accumulator battery. (4)

Ans **Discharging:**

At the anode, the lead atoms release two electrons each to be oxidized to Pb^{2+} ions, which combine with SO_4^{2-} ions present in the electrolyte and get deposited on the anode as $PbSO_4$.

At the cathode,

$$PbO_{2(s)} + 4H^+(aq) + SO_4^{2-}{}_{(aq)} + 2e \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)} \quad \text{(reduction)}$$

At the anode,

$$Pb_{(s)} + SO_4^{2-}{}_{(aq)} \longrightarrow PbSO_{4(s)} + 2e \quad \text{(oxidation)}$$

The electrons released pass round an external circuit as an electric current to be used for starting the engine of a vehicle, for lighting up of car lights and so on.

At the cathode, the electrons from the anode are accepted by PbO_2 and hydrogen ions from the electrolyte then undergo a redox reaction to produce lead ions and water as follows:

The Pb^2 ions then combine with the SO_4^2 ions and they both deposit at the cathode as $PbSO_4$. When both electrodes are completely covered with $PbSO_4$ deposits, the cell will cease to discharge any more current until it is recharged. The overall reaction is:

$$Pb_{(s)} + PbO_{2(s)} + 4H^+_{(aq)} + 2SO_4^{2-}{}_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$

A typical 12-V car battery has six cells connected in series. Each delivers 2V. Each cell contains two lead grids packed with the electrode materials. The anode is spongy lead, and cathode is powered PbO_2. The grid is immersed in an electrolytic solution of $\approx 3.2\ M\ H_2SO_4$ (30%). Fibre glass sheets between the grids prevent shorting by accidental physical contact. When the cell is discharged, it generates electrical energy as a voltaic cell.

Recharging:

During the process of recharging, the anode and the cathode of the external electrical source are connected to the anode and the cathode of the cell, respectively. The redox reactions at the respective electrodes are then reversed. These reactions are summarized as follows:

At anode

$$PbSO_{4(s)} + 2e \rightarrow Pb_{(s)} + SO_4^{2-}{}_{(aq)} \quad \text{(reduction)}$$

At cathode

$$PbSO_{4(s)} + 2H_2O \rightarrow PbO_{2(s)} + 4H^+_{(aq)} + SO_4^{2}{}_{(aq)}\ 2e^- \quad \text{(oxidation)}$$

The overall reaction is

$$2PbSO_{4(s)} + 2H_2O \rightarrow Pb_{(s)} + PbO_{2(s)} + 4H^+_{(aq)} + 2SO_4^{2-}{}_{(aq)}$$

During the process of discharging, the concentration of the acid falls decreasing its density to 1.15 g cm^3. After recharging, the acid is concentrated again bringing its density to its initial value of 1.25 g cm^3. At the same time, the voltage of the battery, which has dropped during discharging, return to around 12 volts.

(b) The solubility product of Ag_2CrO_4 is 2.6×10^{-2} at 25°C. Calculate solubility of compound. (4)

Ans As we have,

$$K_{sp} = 2.6 \times 10^{-2}$$

Let 's' moles of Ag_2CrO_4 is dissolved in 1 dm^3 of the solution, then 's' refers molarity or solubility of Ag_2CrO_4.

Now,

$$Ag_2CrO_{4(s)} \rightleftharpoons 2\,Ag^+_{(aq)} + CrO_4^-$$

$$K_{sp} = [Ag^+]^2 [CrO_4^-]$$
$$= (2s)^2(s)$$
$$= 4s^2(s)$$
$$K_{sp} = 4s^3$$
$$2.6 \times 10^{-2} = 4s^3$$
$$\frac{2.6 \times 10^{-2}}{4} = s^3$$
$$\Rightarrow \quad s = \sqrt[3]{\frac{2.6 \times 10^{-2}}{4}}$$
$$s = 0.1866 \text{ mol dm}^{-3}$$

Hence, the solubility of Ag_2CrO_4 is 0.1866 mol dm^{-3}.

Q.9.(a) Define the following terms: (4)
Molarity, Molality, Mole Fraction and Parts per million (PPM).

Ans **(i) Molarity:**

Molarity is number of moles of solute dissolved per dm^3 of solution.

$$\text{Molarity} = \frac{\text{Mass of solute}}{\text{Mol. mass of solute}} \times \frac{1}{\text{volume of solution in dm}^3}$$

(ii) Molality:

Molality is number of moles of solute in 1000 g (1 kg) of solvent.

$$\text{Molality} = \frac{\text{Mass of solute}}{\text{Mol. mass of solute}} \times \frac{1}{\text{Mass of solvent in kg}}$$

(iii) Mole Fraction:

Mole fraction of any component in mixture is ratio of no. of moles of it to total no. of moles of all components present.

$$X_A = \frac{n_A}{n_A + n_B + n_C}$$

(iv) Parts per million:

It is defined as no. of parts of solute per million parts of solution.

$$\text{ppm} = \frac{\text{Mass of solute}}{\text{mass of solution}} \times 10^6 .$$

(b) How light and surface area affect the rate of reaction?

Ans **Surface Area:**

The increased surface area of reactants, increases the possibilities of atoms and molecules of reactants to come in contact with each other and the rates enhance. For example, *Al* foil reacts with NaOH moderately when warmed, but powdered *Al* reacts rapidly with cold NaOH and H_2 is evolved with frothing.

$$2Al + 2NaOH + 6H_2O \longrightarrow 2NaAl(OH)_4 + 3H_2$$

Similarly, $CaCO_3$ in the powder form reacts with dilute H_2SO_4 more efficiently than its big pieces.

Light:

Light consists of photons having definite amount of energies depending upon their frequencies. When the reactants are irradiated, this energy becomes available to them and rates of reactions are enhanced. The reaction of CH_4 and Cl_2 requires light. The reaction between H_2 and Cl_2 at ordinary pressure is negligible in darkness, slow in daylight, but explosive in sunlight. Similarly, light is vital in photosynthesis, and the rate is influenced by light.